

CLAIMS

1. A method of modifying a multi-coordinated metal complex, a salt, a solvate or an enantiomer thereof, said multi-coordinated metal complex comprising (i) at least one
5 multidentate Schiff base ligand comprising an imino group and being coordinated to the metal, in addition to the nitrogen atom of said imino group, through at least one further heteroatom selected from the group consisting of oxygen, sulfur and selenium, and (ii) one or more other ligands, characterized in that the method comprises bringing said multi-coordinated metal complex into contact with an acid under conditions such that said acid
10 is able to at least partly cleave a bond between the metal and said at least one multidentate Schiff base ligand (i), and wherein said other ligands (ii) are selected such as to be unable of protonation by said acid under said conditions.
2. A method according to claim 1, characterized in that said conditions include a molar
15 ratio between said acid and said multi-coordinated metal complex being above 1.2 and below 40.
3. A method according to claim 1 or claim 2, characterized in that said conditions include a contact time from 5 seconds to 100 hours.
- 20 4. A method according to any of claims 1 to 3, characterized in that said conditions include a contact temperature from about -50 °C to about +80 °C.
5. A method according to any of claims 1 to 4, characterized in that said other ligands (ii)
25 are not selected from the group consisting of phosphines, amines, arsines and stibines.
6. A method according to any of claims 1 to 5, wherein the pKa of said acid is lower than the pKa of said multidentate Schiff base ligand (ii).
- 30 7. A method according to any of claims 1 to 6, characterized in that at least one of said other ligands (ii) is a constraint steric hindrance ligand having a pKa of at least 15.
8. A method according to any of claims 1 to 7, characterized in that the number of carbon atoms in said at least one multidentate Schiff base ligand (i), between the nitrogen atom of
35 said imino group and said coordinating heteroatom of said at least one multidentate Schiff base ligand (i), is from 2 to 4.

9. A method according to any of claims 1 to 8, characterized in that at least one of said other ligands (ii) is a carbene ligand selected from the group consisting of N-heterocyclic carbenes, alkylidene ligands, vinylidene ligands, indenylidene ligands and allenylidene ligands.
10. A method according to any of claims 1 to 8, characterized in that at least one of said other ligands (ii) is an anionic ligand.
11. A method according to any of claims 1 to 8, characterized in that at least one of said other ligands (ii) is a non-anionic ligand.
12. A method according to any of claims 1 to 11, characterized in that said acid is chlorhydric acid or bromhydric acid.
13. A method according to any of claims 1 to 12, characterized in that said conditions are able to protonate the multidentate Schiff base ligand and decoordinate the nitrogen atom of the imino group of said multidentate Schiff base ligand from the metal.
14. A method according to any of claims 1 to 13, characterized in that said conditions are able to decoordinate the further heteroatom of said multidentate Schiff base ligand from the metal.
15. The reaction product of:
- (a) a multi-coordinated metal complex, a salt, a solvate or an enantiomer thereof, said multi-coordinated metal complex comprising (i) at least one multidentate Schiff base ligand comprising an imino group and being coordinated to the metal, in addition to the nitrogen atom of said imino group, through at least one further heteroatom selected from the group consisting of oxygen, sulfur and selenium, and (ii) one or more other ligands, and
- (b) an acid reacted in a molar ratio above about 1.2 with respect to said multi-coordinated metal complex (a),
- provided that said other ligands (ii) are unable of protonation by said acid.
16. A product according to claim 15, characterized in that said other ligands (ii) are not selected from the group consisting of amines, phosphines, arsines and stibines.

17. A product according to claim 15 or claim 16, characterized in that the pKa of said acid (b) is lower than the pKa of said at least one multidentate Schiff base ligand (i).

5 18. A product according to any of claims 15 to 17, characterized in that the number of carbon atoms in said at least one multidentate Schiff base ligand (i), between the nitrogen atom of said imino group and said heteroatom of said at least one multidentate Schiff base ligand (i), is from 2 to 4.

10 19. A product according to any of claims 15 to 18, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is a constraint steric hindrance ligand having a pKa of at least 15.

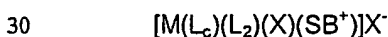
15 20. A product according to any of claims 15 to 19, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is a carbene ligand selected from the group consisting of N-heterocyclic carbenes, alkylidene ligands, vinylidene ligands, indenylidene ligands and allenylidene ligands.

20 21. A product according to any of claims 15 to 19, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is an anionic ligand.

22. A product according to any of claims 15 to 19, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is a non-anionic ligand.

25 23. A product according to any of claims 15 to 22, characterized in that said acid is chlorhydric acid or bromhydric acid.

24. A product according to any of claims 15 to 23, being a monometallic species represented by the general formula:



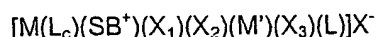
wherein

- M is a metal selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table, preferably a metal selected from ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, copper, chromium, manganese, rhodium, vanadium, zinc, gold, silver, nickel and cobalt;
- 35

- SB^+ is a protonated Schiff base ligand, preferably a protonated bidentate Schiff base ligand;
- L_c is a carbene ligand, preferably selected from the group consisting of alkylidene ligands, vinylidene ligands, indenylidene ligands and allenylidene ligands;
- 5 - L_2 is a non-anionic ligand, preferably other than a phosphine ligand;
- X is an anionic ligand; and
- X^- is an anion,

salts, solvates and enantiomers thereof.

- 10 25. A product according to any of claims 15 to 23, being a bimetallic species represented by the general formula:

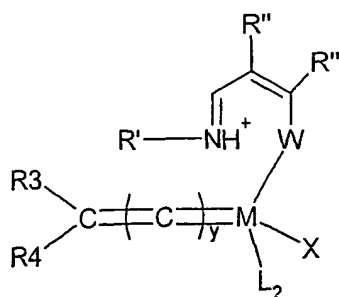


wherein

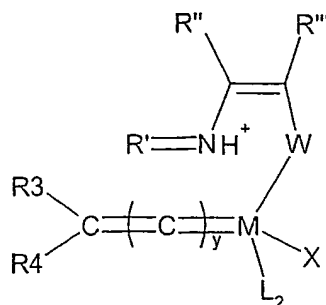
- M and M' are each a metal independently selected from the group consisting of
- 15 groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table, preferably a metal selected from ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, copper, chromium, manganese, rhodium, vanadium, zinc, gold, silver, nickel and cobalt;
- SB^+ is a protonated Schiff base ligand, preferably a protonated bidentate Schiff
- 20 base ligand;
- L_c is a carbene ligand, preferably selected from the group consisting of alkylidene ligands, vinylidene ligands, indenylidene ligands and allenylidene ligands;
- L is a non-anionic ligand, preferably other than a phosphine ligand;
- X_1 , X_2 and X_3 are each independently selected from anionic ligands; and
- 25 - X^- is an anion,

salts, solvates and enantiomers thereof.

26. A product according to any of claims 15 to 23, being a cationic monometallic species being represented by the general formula (VI):



or a cationic monometallic species being represented by the general formula (VII):



wherein

- M is a metal selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table, preferably a metal selected from ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, copper, chromium, manganese, rhodium, vanadium, zinc, gold, silver, nickel and cobalt;
- W is selected from the group consisting of oxygen, sulphur, selenium, NR^{''''}, PR^{''''}, AsR^{''''} and SbR^{''''};
- R'', R''' and R^{''''} are each a radical independently selected from the group consisting of hydrogen, C₁₋₆ alkyl, C₃₋₈ cycloalkyl, C₁₋₆ alkyl-C₁₋₆ alkoxysilyl, C₁₋₆ alkyl-aryloxysilyl, C₁₋₆ alkyl-C₃₋₁₀ cycloalkoxysilyl, aryl and heteroaryl, or R'' and R''' together form an aryl or heteroaryl radical, each said radical (when different from hydrogen) being optionally substituted with one or more, preferably 1 to 3, substituents R₅ each independently selected from the group consisting of halogen atoms, C₁₋₆ alkyl, C₁₋₆ alkoxy, aryl, alkylsulfonate, arylsulfonate, alkylphosphonate, arylphosphonate, C₁₋₆ alkyl-C₁₋₆ alkoxysilyl, C₁₋₆ alkyl-aryloxysilyl, C₁₋₆ alkyl-C₃₋₁₀ cycloalkoxysilyl, alkylammonium and arylammonium;
- R' is either as defined for R'', R''' and R^{''''} when included in a compound having the general formula (IA) or, when included in a compound having the general formula (IB), is selected from the group consisting of C₁₋₆ alkylene and C₃₋₈ cycloalkylene, the said alkylene or cycloalkylene group being optionally substituted with one or more substituents R₅;
- L₂ is a non-anionic ligand, preferably other than a phosphine ligand;
- X is an anionic ligand;
- R₃ and R₄ are each hydrogen or a radical selected from the group consisting of C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₁₋₂₀ carboxylate, C₁₋₂₀ alkoxy, C₂₋₂₀ alkenyloxy, C₂₋₂₀ alkynyloxy, aryl, aryloxy, C₁₋₂₀ alkoxycarbonyl, C₁₋₂₀ alkylthio, C₁₋₂₀

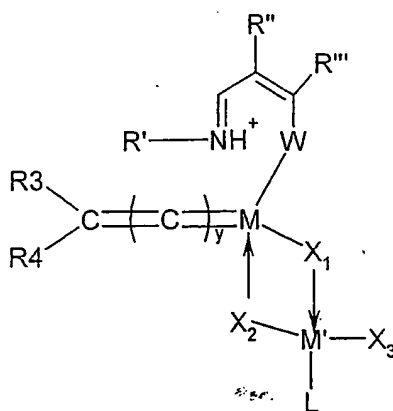
alkylsulfonyl; C₁₋₂₀ alkylsulfinyl C₁₋₂₀ alkylsulfonate, arylsulfonate, C₁₋₂₀ alkylphosphonate, arylphosphonate, C₁₋₂₀ alkylammonium and arylammonium;

- R' and one of R₃ and R₄ may be bonded to each other to form a bidentate ligand;
- R''' and R'''' may be bonded to each other to form an aliphatic ring system including a heteroatom selected from the group consisting of nitrogen, phosphorous, arsenic and antimony;
- R₃ and R₄ together may form a fused aromatic ring system, and
- y represents the number of sp₂ carbon atoms between M and the carbon atom bearing R₃ and R₄ and is an integer from 0 to 3 inclusive,

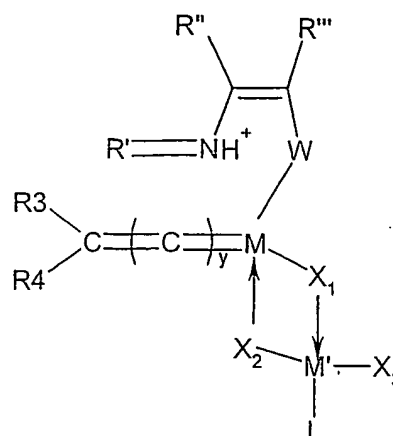
10 salts, solvates and enantiomers thereof, and said cationic species being associated with an anion.

27. A product according to any of claims 15 to 23, being a cationic bimetallic species being represented by the general formula (X):

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or a cationic bimetallic species being represented by the general formula (XI):



wherein

- M and M' are each a metal independently selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table, preferably a metal selected from ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, copper, chromium, manganese, rhodium, vanadium, zinc, gold, silver, nickel and cobalt;
- W is selected from the group consisting of oxygen, sulphur, selenium, NR''', PR''', AsR''' and SbR''';
- R'', R''' and R'''' are each a radical independently selected from the group consisting of hydrogen, C₁₋₆ alkyl, C₃₋₈ cycloalkyl, C₁₋₆ alkyl-C₁₋₆ alkoxy, C₁₋₆ alkyl-aryloxy, C₁₋₆ alkyl-C₃₋₁₀ cycloalkoxy, aryl and heteroaryl, or R'' and R''' together form an aryl or heteroaryl radical, each said radical (when different from hydrogen) being optionally substituted with one or more, preferably 1 to 3, substituents R₅ each independently selected from the group consisting of halogen atoms, C₁₋₆ alkyl, C₁₋₆ alkoxy, aryl, alkylsulfonate, arylsulfonate, alkylphosphonate, arylphosphonate, C₁₋₆ alkyl-C₁₋₆ alkoxy, C₁₋₆ alkyl-aryloxy, C₁₋₆ alkyl-C₃₋₁₀ cycloalkoxy, alkylammonium and arylammonium;
- R' is either as defined for R'', R''' and R'''' when included in a compound having the general formula (IA) or, when included in a compound having the general formula (IB), is selected from the group consisting of C₁₋₆ alkylene and C₃₋₈ cycloalkylene, the said alkylene or cycloalkylene group being optionally substituted with one or more substituents R₅;
- R₃ and R₄ are each hydrogen or a radical selected from the group consisting of C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₁₋₂₀ carboxylate, C₁₋₂₀ alkoxy, C₂₋₂₀ alkenyloxy, C₂₋₂₀ alkynyloxy, aryl, aryloxy, C₁₋₂₀ alkoxycarbonyl, C₁₋₆ alkylthio, C₁₋₂₀

alkylsulfonyl, C₁₋₂₀ alkylsulfinyl C₁₋₂₀ alkylsulfonate, arylsulfonate, C₁₋₂₀ alkylphosphonate, arylphosphonate, C₁₋₂₀ alkylammonium and arylammonium;

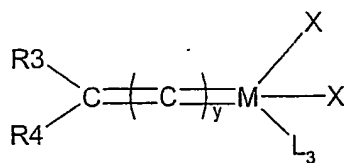
- R' and one of R₃ and R₄ may be bonded to each other to form a bidentate ligand;
- R''' and R''' may be bonded to each other to form an aliphatic ring system including a heteroatom selected from the group consisting of nitrogen, phosphorous, arsenic and antimony;
- R₃ and R₄ together may form a fused aromatic ring system, and
- y represents the number of sp₂ carbon atoms between M and the carbon atom bearing R₃ and R₄ and is an integer from 0 to 3 inclusive,

- X₁, X₂ and X₃ are each independently selected from anionic ligands; and

- L is a non-anionic ligand, preferably other than a phosphine ligand,

including salts, solvates and enantiomers thereof.

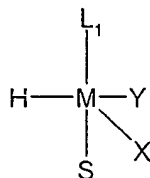
28. A product according to any of claims 15 to 23, being a monometallic complex represented by the general formula (VIII):



wherein

- M is a metal selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table, preferably a metal selected from ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, copper, chromium, manganese, rhodium, vanadium, zinc, gold, silver, nickel and cobalt;
- X is an anionic ligand;
- R₃ and R₄ are each hydrogen or a radical selected from the group consisting of C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₁₋₂₀ carboxylate, C₁₋₂₀ alkoxy, C₂₋₂₀ alkenyloxy, C₂₋₂₀ alkynyloxy, aryl, aryloxy, C₁₋₂₀ alkoxycarbonyl, C₁₋₈ alkylthio, C₁₋₂₀ alkylsulfonyl, C₁₋₂₀ alkylsulfinyl C₁₋₂₀ alkylsulfonate, arylsulfonate, C₁₋₂₀ alkylphosphonate, arylphosphonate, C₁₋₂₀ alkylammonium and arylammonium;
- R₃ and R₄ together may form a fused aromatic ring system;
- y represents the number of sp₂ carbon atoms between M and the carbon atom bearing R₃ and R₄ and is an integer from 0 to 3 inclusive;
- X' is a anionic ligand; and
- L₃ is a non-anionic ligand, other than a phosphine ligand, salts, solvates and enantiomers thereof.

29. A product according to any of claims 15 to 23, being a monometallic complex represented by the general formula (IX):



wherein:

- 5 - M is a metal selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table, preferably a metal selected from ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, copper, chromium, manganese, rhodium, vanadium, zinc, gold, silver, nickel and cobalt;
 - X is an anionic ligand;
 - 10 - S is a solvent;
 - Y is a solvent or Y is CO when S is an alcohol; and
 - L₁ is a non-anionic ligand, preferably other than a phosphine ligand,
- salts, solvates and enantiomers thereof.

15 30. A product according to any of claims 15 to 23, at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is a solvent S and said complex (a) is a cationic species associated with an anion A.

20 31. A product according to any of claims 15 to 23, characterized in that said multi-coordinated metal complex (a) is a bimetallic complex.

32. A product according to claim 31, characterized in that one metal of said bimetallic complex is penta-coordinated with said at least one multidentate Schiff base ligand (i) and with said one or more other ligands (ii), and the other metal is tetra-coordinated with one
25 or more neutral ligands and one or more anionic ligands.

33. A product according to claim 31, characterized in that each metal of said bimetallic complex is hexa-coordinated with said at least one multidentate Schiff base ligand (i) and with said one or more other ligands (ii).

34. A product according to claim 31, characterized in that the two metals of the bimetallic complex are the same.
35. A product according to claim 31, characterized in that the two metals of the bimetallic
5 complex are different.
36. A product according to any of claims 15 to 23, characterized in that said multi-coordinated metal complex (a) is a monometallic complex.
- 10 37. A product according to any of claims 15 to 23, characterized in that the metal of said multi-coordinated metal complex (a) is a transition metal selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table.
- 15 38. A product according to any of claims 15 to 23, characterized in that said metal is selected from the group consisting of ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, technetium, lanthanum, copper, chromium, manganese, palladium, platinum, rhodium, vanadium, zinc, cadmium, mercury, gold, silver, nickel and cobalt.
- 20 39. A product according to any of claims 15 to 23, characterized in that said multi-coordinated metal complex (a) is a penta-coordinated metal complex or a tetra-coordinated metal complex.
- 25 40. A product according to claim 39, characterized in that said at least one multidentate Schiff base ligand (i) is a bidentate ligand and said multi-coordinated metal complex (a) comprises two other ligands (ii).
- 30 41. A product according to claim 39, characterized in that said at least one multidentate Schiff base ligand (i) is a tridentate ligand and said multi-coordinated metal complex (a) comprises a single other ligand (iii).
42. A product according to claim 39 or claim 40, characterized in that said at least one multidentate Schiff base ligand (i) has one of the general formulae (IA) and (IB) referred to in figure 1, wherein:
- Z is selected from the group consisting of oxygen, sulfur and selenium;
 - 35 - R'' and R''' are each a radical independently selected from the group consisting of hydrogen, C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, C₁₋₆ alkyl-C₁₋₆ alkoxyethyl, C₁₋₆ alkyl-

- aryloxysilyl, C₁₋₆ alkyl-C₃₋₁₀ cycloalkoxysilyl, aryl and heteroaryl, or R" and R"' together form an aryl or heteroaryl radical, each said radical being optionally substituted with one or more, preferably 1 to 3, substituents R₅ each independently selected from the group consisting of halogen atoms, C₁₋₆ alkyl, C₁₋₆ alkoxy, aryl, alkylsulfonate, arylsulfonate, alkylphosphonate, arylphosphonate, C₁₋₆ alkyl-C₁₋₆ alkoxysilyl, C₁₋₆ alkyl-aryloxysilyl, C₁₋₆ alkyl-C₃₋₁₀ cycloalkoxysilyl, alkylammonium and arylammonium;
- R' is either as defined for R" and R"' when included in a compound having the general formula (IA) or, when included in a compound having the general formula (IB), is selected from the group consisting of C₁₋₇ alkylene and C₃₋₁₀ cycloalkylene, the said alkylene or cycloalkylene group being optionally substituted with one or more substituents R₅.

43. A product according to claim 39, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is a derivative, wherein one or more hydrogen atoms is substituted with a group providing constraint steric hindrance, of a N-heterocyclic carbene selected from the group consisting of imidazol-2-ylidene, dihydroimidazol-2-ylidene, oxazol-2-ylidene, triazol-5-ylidene, thiazol-2-ylidene, bis(imidazol-2-ylidene), bis(imidazolidin-2-ylidene), pyrrolylidene, pyrazolylidene, dihydropyrrolylidene, pyrrolylidinylidene and benzo-fused derivatives thereof, or a non-ionic phosphatane superbase.

44. A product according to claim 39, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is an anionic ligand selected from the group consisting of C₁₋₂₀ alkyl, C₁₋₂₀ alkenyl, C₁₋₂₀ alkynyl, C₁₋₂₀ carboxylate, C₁₋₂₀ alkoxy, C₁₋₂₀ alkenyloxy, C₁₋₂₀ alkynyloxy, aryl, aryloxy, C₁₋₂₀ alkoxycarbonyl, C₁₋₆ alkylthio, C₁₋₂₀ alkylsulfonyl, C₁₋₂₀ alkylsulfinyl, C₁₋₂₀ alkylsulfonate, arylsulfonate, C₁₋₂₀ alkylphosphonate, arylphosphonate, C₁₋₂₀ alkylammonium, arylammonium, halogen atoms and cyano.

45. A product according to claim 39, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is a carbene ligand represented by the general formula $=[C=]_yCR_3R_4$, wherein:

- y is an integer from 0 to 3 inclusive, and
- R₃ and R₄ are each hydrogen or a hydrocarbon radical selected from the group consisting of C₁₋₂₀ alkyl, C₁₋₂₀ alkenyl, C₁₋₂₀ alkynyl, C₁₋₂₀ carboxylate, C₁₋₂₀ alkoxy, C₁₋₂₀ alkenyloxy, C₁₋₂₀ alkynyloxy, aryl, aryloxy, C₁₋₂₀ alkoxycarbonyl, C₁₋₆ alkylthio,

C₁₋₂₀ alkylsulfonyl, C₁₋₂₀ alkylsulfinyl C₁₋₂₀ alkylsulfonate, arylsulfonate, C₁₋₂₀ alkylphosphonate, arylphosphonate, C₁₋₂₀ alkylammonium and arylammonium; or R₃ and R₄ together may form a fused aromatic ring system.

- 5 46. A product according to claim 45, characterized in that R₃ and R₄ together form a fused aromatic ring system such that said other ligand (ii) of said multi-coordinated metal complex (a) is a phenylindenylidene ligand.
- 10 47. A product according to claim 39, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is a non-anionic unsaturated ligand L¹ selected from the group consisting of aromatic and unsaturated cycloaliphatic groups, preferably aryl, heteroaryl and C₄₋₂₀ cycloalkenyl groups, the said aromatic or unsaturated cycloaliphatic group being optionally substituted with one or more C₁₋₇ alkyl groups or electron-withdrawing groups such as, but not limited to, halogen, nitro, 15 cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide.
- 20 48. A product according to claim 39, characterized in that at least one of said other ligands (ii) of said multi-coordinated metal complex (a) is a non-anionic ligand L² selected from the group consisting of C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, arylalkyl and heterocyclic, the said group being optionally substituted with one or more preferably electron-withdrawing substituents such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide.
- 25 49. A product according to claim 39, characterized in that said at least one multidentate Schiff base ligand (i) is a tetradentate ligand and said multi-coordinated metal complex (a) comprises one or two other ligands (ii) being non-anionic ligands L⁷ selected from the group consisting of aromatic and unsaturated cycloaliphatic groups, preferably 30 aryl, heteroaryl and C₄₋₂₀ cycloalkenyl groups, wherein the said aromatic or unsaturated cycloaliphatic group is optionally substituted with one or more C₁₋₇ alkyl groups or electron-withdrawing groups such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide.
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50. A product according to claim 15, wherein said acid (b) is an acid generated *in situ* from a photoacid generator.
51. A product according to claim 15, comprising the product of at least partial cleavage of
 5 a bond between the metal and said at least one multidentate Schiff base ligand (i).
52. A catalytic system comprising:
- (a) as the main catalytic species, a reaction product according to any of claims 15 to 51, and
 - 10 (b) one or more second catalyst components being selected from the group consisting of Lewis acid co-catalysts (b_1), catalyst activators (b_2), and initiators having a radically transferable atom or group (b_3).
53. A catalytic system according to claim 52, wherein the second catalyst component
 15 includes a co-catalyst (b_1) selected from the group consisting of boron trihalides; phosphorus trihalides; trialkylboron compounds; triarylboron compounds; organoaluminum compounds; magnesium dihalides; aluminum trihalides; tin tetrachloride; titanium or vanadium trihalides or tetrahalides or tetraalkoxides; antimony and bismuth pentahalides.
- 20 54. A catalytic system according to claim 52, wherein the second catalyst component includes, as a catalyst activator (b_2), a diazo compound.
55. A catalytic system according to claim 52, wherein the second catalyst component
 25 includes, as an initiator having a radically transferable atom or group (b_3), a compound having the formula $R_{35}R_{36}R_{37}CX_1$, wherein:
- X_1 is selected from the group consisting of halogen, OR_{38} (wherein R_{38} is selected from C_{1-20} alkyl, polyhalo C_{1-20} alkyl, C_{2-20} alkynyl (preferably acetylenyl), C_{2-20} alkenyl (preferably vinyl), phenyl optionally substituted with 1 to 5 halogen atoms or C_{1-7} alkyl groups and phenyl-substituted C_{1-7} alkyl), SR_{39} , $OC(=O)R_{39}$, $OP(=O)R_{39}$, $OP(=O)(OR_{39})_2$, $OP(=O)OR_{39}$, $O-N(R_{39})_2$ and $S-C(=S)N(R_{39})_2$, wherein R_{39} is aryl or C_{1-20} alkyl, or where an $N(R_{39})_2$ group is present, the two R_{39} groups may be joined to form a 5-, 6- or 7-membered heterocyclic ring (in accordance with the definition of heteroaryl above), and
 - 30 - R_{35} , R_{36} and R_{37} are each independently selected from the group consisting of hydrogen, halogen, C_{1-20} alkyl (preferably C_{1-6} alkyl), C_{3-8} cycloalkyl, $C(=O)R_{40}$,
 - 35

(wherein R_{40} is selected from the group consisting of C_{1-20} alkyl, C_{1-20} alkoxy, aryloxy or heteroaryloxy), $C(=O)NR_{41}R_{42}$ (wherein R_{41} and R_{42} are independently selected from the group consisting of hydrogen and C_{1-20} alkyl or R_{41} and R_{42} may be joined together to form an alkylene group of 2 to 5 carbon atoms), $COCl$, OH ,
 5 CN , C_{2-20} alkenyl (preferably vinyl), C_{2-20} alkynyl, oxiranyl, glycidyl, aryl, heteroaryl, arylalkyl and aryl-substituted C_{2-20} alkenyl.

56. A supported catalyst, comprising:

- 10 (a) a catalytically active reaction product according to any of claims 15 to 51, or a catalytic system according to claim 52, and
 (b) a supporting amount of a carrier suitable for supporting said catalytically active product or catalytic system (a).

15 57. A method of performing an olefin or acetylene metathesis reaction or a reaction involving the transfer of an atom or group to an ethylenically or acetylenically unsaturated compound or another reactive substrate in the presence of a catalytic component, wherein the said catalytic component comprises a product according to any of claims 15 to 51 or a catalytic system according to any of claims 52 to 55.

20 58. A method according to claim 57, wherein said reaction involving the transfer of an atom or group to an olefin or another reactive substrate is selected from the group consisting of:

- atom or group transfer radical polymerisation of one or more radically (co)polymerisable monomers, especially mono- and diethylenically unsaturated monomers;
 25
- atom transfer radical addition of a polyhalomethane having the formula CX_nH_{4-n} , wherein X is halogen and n is an integer from 2 to 4, onto an ethylenically unsaturated compound to produce the corresponding saturated polyhalogenated adduct;
- 30 - vinylation reaction of a mono- or di-alkyne with a mono- or di-carboxylic acid to produce alk-1-enyl esters or enol esters or Markovnikov adducts or anti-Markovnikov adducts or mixtures thereof;
- cyclopropanation of an α -ethylenically unsaturated compound for producing an organic compound having one or more cyclopropane structural units;
- 35 - quinoline synthesis through oxidative cyclisation of 2-aminobenzyl alcohol with ketones;

- epoxidation of α -ethylenically unsaturated compounds for producing epoxides;
- oxidation of organic compounds including the oxidation of saturated hydrocarbons for producing alcohols, or sulfides for producing sulfoxides and sulfones, or phosphines for producing phosphonates, or alcohols and aldehydes for producing carboxylic acids;
- cyclopropenation of an alkyne for producing an organic compound having one or more cyclopropene structural units;
- hydrocyanation of α -ethylenically unsaturated compounds for producing saturated nitriles, or alkynes for producing unsaturated nitriles, or α,β -unsaturated aldehydes or ketones for producing β -cyano carbonyl compounds;
- hydrosilylation of olefins for producing saturated silanes, or alkynes for producing unsaturated silanes, or ketones for producing silyl ethers, or trimethylsilylcyanation of aldehydes for producing cyanohydrin trimethylsilyl ethers;
- aziridination of imines or alkenes for producing organic compounds having one or more aziridine structural units;
- hydroamidation of olefins for producing saturated amides;
- hydrogenation of olefins for producing alkanes, or ketones for producing alcohols;
- aminolysis of olefins for producing saturated primary or secondary amines;
- isomerisation of alcohols, preferably allylic alcohols, for producing aldehydes;
- Grignard cross-coupling of alkyl or aryl halides for producing alkanes or arylalkanes;
- hydroboration of olefins for producing alkylboranes and trialkylboranes;
- hydride reduction of aldehydes and ketones for producing alcohols;
- aldol condensation of saturated carboxyl compounds for producing α,β -unsaturated carboxyl compounds or β -hydroxycarbonyl compounds, and intramolecular aldol condensation of dialdehydes or diones for producing cyclic α,β -unsaturated carboxyl compounds;
- Michael addition of a ketone or a β -dicarbonyl compound onto an α,β -unsaturated carboxyl compound for producing saturated polycarboxyl compounds;
- Robinson annulation for producing saturated polycyclic carboxyl compounds;
- Heck reactions of an aryl halide or a 1-hetero-2,4-cyclopentadiene or a benzo-fused derivative thereof with an α -ethylenically unsaturated compound for producing arylalkenes or heteroarylalkenes;
- codimerisation of alkenes for producing higher saturated hydrocarbons or alkynes for producing higher alkenes;
- hydroxylation of olefins for producing alcohols;

- hydroamination of olefins and alkynes for producing amines;
- alkylation, preferably allylic alkylation, of ketones for producing alkylated ketones, preferably allylic ketones; and
- Diels-Alder reactions such as the cycloaddition of a conjugated diene onto an α -ethylenically unsaturated compound for producing optionally substituted cyclohexenes, or the cycloaddition of furan onto an α -ethylenically unsaturated compound for producing optionally substituted 7-oxanorbornenes.

59. A method according to claim 57, wherein the said metathesis reaction is the ring-opening metathesis polymerisation of strained cyclic olefins.

60. A method according to claim 57, wherein the catalytic component is supported on a carrier.

61. A method according to claim 60, wherein the said carrier is selected from the group consisting of porous inorganic solids, such as amorphous or paracrystalline materials, crystalline molecular sieves and modified layered materials including one or more inorganic oxides, and organic polymer resins.